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# Iterative CI general singles and doubles (ICIGSD) method for calculating the exact wave functions of the ground and excited states of molecules

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The iterative configuration-interaction general singles and doubles (ICIGSD) method was applied to various closed- and open-shell electronic states of molecules within finite basis sets and was shown to give the exact results that are identical to the full CI ones. The structure of the ICIGSD is unique among the ICI formalisms, that is, the singularity problem intrinsic to atomic and molecular Hamiltonians can be avoided. The convergence of the ICIGSD method was fairly good regardless of the characters of the electronic states and the qualities of the basis sets; only several iterations were enough for obtaining microhartree accuracy. These favorable properties are attributed to the unique GSD structure. The present method was shown to be applicable to various spin states and to quasidegenerate states appearing in bond dissociation process. We have also applied the ICIGSD-CI method to calculate the excited states simultaneously. We have confirmed that the ICIGSD-CI method is accurate for calculating the excited states the symmetries of which are not only similar to but also different from that of the ground state. © 2005 American Institute of Physics.

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## I. INTRODUCTION

Establishing a method for solving the Schrödinger equation (SE) is a central theme in theoretical chemistry.<sup>1</sup> For this purpose, we have studied the structure of the exact wave function<sup>2-8</sup> and proposed the iterative configuration-interaction (ICI) method<sup>2,3</sup> and the simplest extreme coupled-cluster (SECC) method<sup>4</sup> as the methods to generate the functions having the structure of the exact wave function. When the variables included in these functions are optimized by the variational principle, it gives the exact energy and the exact wave function that are the solution of the SE. For finite-basis approximation, the same method gives the results identical to the full CI (FCI). Such exactness has been confirmed numerically in both analytical and basis-set expansion approaches for harmonic oscillator<sup>3-5</sup> and atomic and molecular systems.<sup>6-8</sup>

Historically, Horn and Weinstein, Kosloff and Tal-Ezer, Cioslowski, and others considered to solve the time-dependent SE on the imaginary time axis.<sup>9</sup> Huang *et al.*<sup>10</sup> proposed the surplus function method for the variational Monte Carlo calculations. Nooijen<sup>11</sup> considered to solve the coupled cluster with general singles and doubles variables (CCGSD) with the density equation<sup>12</sup> that is equivalent with the SE. The present author considered independently a possibility of the exactness of the CCGSD and reached a nega-

tive conclusion.<sup>2</sup> He further considered this subject and showed that the CCGSD is not guaranteed to be exact, again, but its possibility was not excluded because of its highly nonlinear nature.<sup>4</sup> Nevertheless, this possibility has received a lot of interest by many authors.<sup>13-18</sup>

The true solution of the SE is accessible only with an analytical method.<sup>8</sup> In a finite-basis approximation, FCI is the best possible solution but it is far from the true solution of the SE because of the basis-set incompleteness. Nevertheless, we call even the FCI solution as exact, since it is traditionally done so. In the analytical approach, a problem in atomic and molecular calculations was the singularity problem caused by the Coulombic potential involved in the Hamiltonian.<sup>6,8</sup> To circumvent this problem, we proposed the inverse SE<sup>6</sup> and the scaled SE.<sup>8</sup> In particular, the latter approach was quite successful in developing a general method of solving the SE in an analytical form.<sup>8</sup>

In the finite-basis approximation, the singularity problem becomes a bit vague because when you have a Hamiltonian matrix  $\mathbf{H}$ , defined within the basis-set space, you can calculate  $\mathbf{H}^n$  essentially to an arbitrary order, though this is impossible if the basis is complete because then  $(\mathbf{H}^n)_{ij} = \langle i | \mathbf{H}^n | j \rangle$  and the integral in the right-hand side can diverge when  $n \geq 3$ .<sup>8</sup> When the basis is far from complete, the calculation may proceed without much difficulty,<sup>7</sup> but it is due to the incompleteness of the basis set. We have already shown that by introducing the inverse Hamiltonian<sup>6</sup> and the scaled Hamiltonian,<sup>8</sup> the singularity problem can be eliminated.

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The purpose of this paper is to show a special merit of the ICIGSD method for calculating the exact wave function. The merit is twofold: one is the dissolution of the singularity problem and the other is the rapid convergence. In the ICIGSD method, we start from the second-quantized Hamiltonian and introduce the GSD number of variables in the ICI formalism. This makes it possible to formulate the ICIGSD method to be free from the singularity problem. We have shown in the previous paper<sup>7</sup> that when we perform the simplest ICI (SICI) and ICI3, where the numbers of the variables are one and three, respectively, the convergence to the exact wave function is slow; 30–40 iterations for minimal basis and 40–70 iterations for double-zeta basis for getting the energy correct to eight decimal figures. In the ICIGSD presented here, the convergence is much faster than in the SICI and ICI3 given before.

Another purpose of this paper is to show the application of the ICIGSD method to molecular excited states, which was not done in the former calculations with the SICI and ICI3 methods.<sup>7</sup> We have proposed in Paper II<sup>3</sup> three methods of calculating the excited states based on the ICI formalism and these methods were applied to the harmonic oscillator.<sup>5</sup> In this paper, we apply the method B proposed previously<sup>3</sup> to molecular systems and calculate the excited states having the symmetries not only similar to but also different from that of the ground states.

## II. METHOD

### A. ICIGSD with integral-free and integral-including algorithms

First we briefly review the ICIGSD method.<sup>2,3</sup> Originally, the ICI method was introduced in the GSD formalism given below.<sup>2</sup> The Hamiltonian of the system is written in the second-quantized form as

$$H = \sum_{pr} v_p^r a_r^\dagger a_p + \sum_{pqrs} w_{pq}^{rs} a_r^\dagger a_s^\dagger a_q a_p, \quad (1)$$

where  $a_r^\dagger$  and  $a_p$  are the creation and annihilation operators, respectively, and  $p, q, r, s$  run over all occupied and unoccupied orbitals. The integrals  $v_p^r$  and  $w_{pq}^{rs}$  represent one- and two-electron integrals. The energy associated to the wave function  $\Psi$  is defined by

$$\langle \Psi | H - E | \Psi \rangle = 0. \quad (2)$$

It was shown previously<sup>2</sup> that the wave function  $\Psi$  is exact when the following equations are satisfied for all the indices  $p, q, r, s$ ;

$$\langle \Psi | (H - E) a_r^\dagger a_p | \Psi \rangle = 0, \quad (3)$$

$$\langle \Psi | (H - E) a_r^\dagger a_s^\dagger a_q a_p | \Psi \rangle = 0. \quad (4)$$

Based on this theorem, the ICIGSD method was introduced in Paper I<sup>2</sup> for calculating the exact wave function. It is defined in a recursion form as

$$\Psi_{n+1} = (1 + T_n) \Psi_n, \quad (5)$$

where  $T_n$  is the GSD operator given by,

$$T_n = \sum_{pr} {}^n C_p^r a_r^\dagger a_p + \sum_{pqrs} {}^n C_{pq}^{rs} a_r^\dagger a_s^\dagger a_q a_p, \quad (6)$$

where  ${}^n C_p^r$  and  ${}^n C_{pq}^{rs}$  are the variables associated to the singles and doubles operators. In  $T_n$ , only the totally symmetric one- and two-electron operators were included. The variables  ${}^n C_p^r$  and  ${}^n C_{pq}^{rs}$  in  $T_n$  are determined by solving the secular equation,

$$\langle \Psi_{n+1} | (H - E) | \Psi_n \rangle = 0, \quad (7a)$$

$$\langle \Psi_{n+1} | (H - E) a_r^\dagger a_p | \Psi_n \rangle = 0, \quad (7b)$$

$$\langle \Psi_{n+1} | (H - E) a_r^\dagger a_s^\dagger a_q a_p | \Psi_n \rangle = 0, \quad (7c)$$

with the size of the general singles and doubles (GSD). When the convergence is achieved, the ICIGSD wave function satisfies Eqs. (3) and (4), and therefore it is exact. We call the above formulation of the GSD method as *integral-free algorithm*, since no molecular integrals are included in the  $T_n$  operator. Note that ICI satisfies size consistency because it is exact.<sup>2</sup>

A slightly different formulation of the ICIGSD is possible based on the general definition of the ICI theory.<sup>3</sup> In the general context of the ICIND theory,<sup>3</sup> where ND stands for the number of division of the Hamiltonian, we first divide the Hamiltonian into the GSD parts and define the variable operator  $S$  by assigning a variable to each divided element. Namely, referring to the second-quantized Hamiltonian given in Eq. (1), we define the variable operator  $S$  as

$$S_n = \sum_{pr} {}^n c_p^r v_p^r a_r^\dagger a_p + \sum_{pqrs} {}^n c_{pq}^{rs} w_{pq}^{rs} a_r^\dagger a_s^\dagger a_q a_p \quad (8)$$

and define the ICIGSD theory by

$$\Psi_{n+1} = (1 + S_n) \Psi_n. \quad (9)$$

The secular equation for this ICIGSD is

$$\langle \Psi_{n+1} | (H - E) | \Psi_n \rangle = 0, \quad (10a)$$

$$\langle \Psi_{n+1} | (H - E) v_p^r a_r^\dagger a_p | \Psi_n \rangle = 0, \quad (10b)$$

$$\langle \Psi_{n+1} | (H - E) w_{pq}^{rs} a_r^\dagger a_s^\dagger a_q a_p | \Psi_n \rangle = 0. \quad (10c)$$

The latter formulation differs from the former one simply in the presence of the integrals  $v_p^r$  and  $w_{pq}^{rs}$  in the one- and two-electron parts. These integrals can be taken off without affecting the result, simply by redefining the variable operators as  ${}^n C_p^r = {}^n c_p^r v_p^r$  and  ${}^n C_{pq}^{rs} = {}^n c_{pq}^{rs} w_{pq}^{rs}$  and by dividing Eqs. (10b) and (10c) by  $v_p^r$  and  $w_{pq}^{rs}$ , respectively. The difference of these two formulations is thus very small, but as will be seen later, the effect is very big numerically in the actual calculations. We therefore call this latter formulation as *integral-including algorithm*, in contrast to the integral-free algorithm based on Eqs. (5) and (6). Since the integrals given in Eqs. (10b) and (10c) include three-time products of the integrals  $v_p^r$  and  $w_{pq}^{rs}$ , respectively, the singularity problem may appear<sup>8</sup> and cause a difficulty in the integral-including algorithm.

Finally, we note that the integral-free formulation is possible only for the GSD case based on the second-quantized

Hamiltonian given in Eq. (1). In the general ICIND method based on the ordinary Hamiltonian in the coordinate representation, only the integral-including formulation is possible.

## B. ICIGSD-CI for excited states

Next, we explain the ICI-CI method, which is the method for calculating the excited states simultaneously with the ground state. This method was called method B in Paper II<sup>3</sup> and the calculated excited states are not guaranteed to be exact, though they satisfy some necessary conditions of the excited states. On the other hand, method A gives the “exact” excited state, though only one solution is calculated at a time.

When we obtain the exact ground-state wave function  $\Psi_g$  by the ICIGSD method, we have at the same time the GSD number ( $N_{\text{GSD}}$ ) of good basis functions for the excited states, which we designate as  $\{\Phi_K\}$ ,

$$\{\Phi_K\} = \{a_r^\dagger a_p |\Psi_g\rangle, a_r^\dagger a_s^\dagger a_q a_p |\Psi_g\rangle\} \quad (K = 1, \dots, N_{\text{GSD}}), \quad (11)$$

where  $K$  represents  $p, r$  and  $p, q, r, s$ . Eq. (7) implies that these excited functions satisfy the Brillouin-orthogonality with the exact ground state,

$$\langle \Psi_g | (H - E) | \Phi_K \rangle = 0, \quad (12)$$

and this relation means that the functions  $\{\Phi_K\}$  constitute the basis of the excited states.<sup>19</sup> Then, we expand our excited state by a linear combination of these functions as

$$\Psi_e = \sum_{K=1}^{N_{\text{GSD}}} d_K \Phi_K, \quad (13)$$

which is written in a more explicit form as

$$\Psi_e = \left( \sum_{pr} d_{pr}^\dagger a_r^\dagger a_p + \sum_{pqrs} d_{pqrs}^\dagger a_r^\dagger a_s^\dagger a_q a_p \right) \Psi_g. \quad (14)$$

This wave function gives a good approximation of the excited states. Comparing Eq. (14) with Eq. (5), you will see, however, that these excited states are nothing but the higher solutions of the converged ICIGSD solutions.<sup>3</sup> Eq. (14) has a realistic meaning when the symmetry of the excited states is different from that of the ground state. For example, we can generate triplet excited states using Eq. (14) from the singlet ground state  $\Psi_g$ . Similarly, we can generate ionized and electron-attached states by replacing the GSD excitation operators  $\{R_{ij}\} = \{a_r^\dagger a_p, a_r^\dagger a_s^\dagger a_q a_p\}$  with the ionization operators  $\{R_{ij}\} = \{a_r, a_r^\dagger a_q a_p\}$  and the electron-attachment operators  $\{R_{ij}\} = \{a_r^\dagger, a_r^\dagger a_s^\dagger a_p\}$ , respectively.

You find a close similarity of the above formulation with that of the symmetry-adapted-cluster configuration-interaction (SAC-CI) method for the excited states;<sup>19</sup> ICIGSD corresponds to SAC<sup>20</sup> and ICIGSD-CI to SAC-CI.<sup>19</sup> Further, we can get more accurate wave functions by using the ICIGSD-CI general- $R$  method,<sup>3</sup> in which triple and higher operators are included in the  $R$  operators in addition to Eq. (14). This approach was called method C in Paper II<sup>3</sup> and corresponds to the SAC-CI general- $R$  method.<sup>21</sup>

TABLE I. ICIGSD and FCI for  $\text{C}_2\text{H}_4$  with the minimal basis set.<sup>a</sup>

| Hartree-Fock<br>energy<br>(a.u.) | FCI    |                  | ICIGSD |      |                  |
|----------------------------------|--------|------------------|--------|------|------------------|
|                                  | Dim.   | Energy<br>(a.u.) | Iter.  | Dim. | Energy<br>(a.u.) |
| -77.826602                       | 107952 | -77.991647       | 1      | 125  | -77.978734       |
|                                  |        |                  | 2      | 465  | -77.991152       |
|                                  |        |                  | 3      | 532  | -77.991627       |
|                                  |        |                  | 4      | 532  | -77.991645       |
|                                  |        |                  | 5      | 532  | -77.991647       |

<sup>a</sup>ICIGSD is due to the integral-free algorithm.

## C. Details of calculations

In the ICIGSD and ICIGSD-CI calculations, the basic wave functions were expanded by the Slater determinants, and in each iteration, we calculated the functions  $\{a_r^\dagger a_p |\psi_n\rangle, a_r^\dagger a_s^\dagger a_q a_p |\psi_n\rangle\}$  and the Hamiltonian matrix elements between them. The Knowles-Handy algorithm<sup>22</sup> was useful. The present algorithm may be summarized as follows:

- (1) An appropriate initial guess  $|\psi_0\rangle$  is chosen. It was mostly Hartree-Fock.
- (2)  $\{a_r^\dagger a_p |\psi_n\rangle, a_r^\dagger a_s^\dagger a_q a_p |\psi_n\rangle\}$  are calculated for the operators with  $\{v_p^r, w_{pq}^{rs}\}$  in the Hamiltonian nonzero.
- (3) The Hamiltonian and overlap matrices for the basis functions  $\{|\psi_n\rangle, a_r^\dagger a_p |\psi_n\rangle, a_r^\dagger a_s^\dagger a_q a_p |\psi_n\rangle\}$  are calculated.
- (4) The ICIGSD secular equation given by Eq. (7) or (10) is diagonalized.
- (5) The convergence is checked.

After obtaining the ground-state ICIGSD wave function, the ICIGSD-CI wave functions and the secular equation were constructed and solved.

Most calculations were done by the integral-free algorithm, except when remarked. We also carried out the calculations by the integral-including algorithm to see the difference from the calculations with the integral-free algorithm. The coding was done rather straightforwardly and was not aimed to be efficient.

## III. RESULTS

### A. Integral-free versus integral-including algorithms and the convergence behavior

First, we performed the ICIGSD calculations for the singlet ground state using minimal STO-6G basis<sup>23</sup> and double-zeta basis.<sup>24</sup> The minimal basis calculations were done for  $\text{H}_2\text{O}$ ,  $\text{BH}$ ,  $\text{N}_2$ ,  $\text{HCN}$ , acetylene ( $\text{C}_2\text{H}_2$ ), ethylene ( $\text{C}_2\text{H}_4$ ),  $\text{CH}_3\text{F}$ ,  $\text{HCHO}$ ,  $\text{CO}_2$ , and  $\text{O}_3$  and the double-zeta calculations were done for  $\text{Be}$ ,  $\text{LiH}$ ,  $\text{BH}$ ,  $^1\Sigma$  and  $^1\Pi$  states of  $\text{CH}^+$ , and  $\text{HF}$ . In the minimal basis calculations, the  $1s$  orbitals of the second-row atoms were kept as frozen cores. These systems were studied in the previous SICI and ICI3 works<sup>7</sup> and so a direct comparison with the previous result is possible. Note, however, that the dimension here is the number of the Slater determinants, and that of the previous paper<sup>7</sup> was the number of the symmetry-adapted configurations.



TABLE II. ICIGSD with integral-including and integral-free algorithms. Numbers in parenthesis indicate powers of 10. NA means that the diagonalization of ICIGSD failed.

| Molecule iteration               | Integral-including algorithm | Integral-free algorithm |
|----------------------------------|------------------------------|-------------------------|
| O <sub>3</sub> (minimal basis)   |                              |                         |
| H <sub>diag</sub>                | -1.29(-6)--3.34(4)           | -1.04(1)--5.40(2)       |
| 1                                | -223.638944                  | -223.638944             |
| 2                                | -223.677392                  | -223.677406             |
| 3                                | -223.679863                  | -223.679870             |
| 4                                | -223.679968                  | -223.679980             |
| 5                                | -223.679979                  | -223.679983             |
| 6                                | NA                           | -223.679983             |
| 7                                | NA                           | -223.679984 (Conv.)     |
| CH (double zeta)                 |                              |                         |
| H <sub>diag</sub>                | 1.54(1)--5.51(4)             | -1.63(2)--2.45(1)       |
| 1                                | -37.965931                   | -37.965931              |
| 2                                | -37.969372                   | -37.969374              |
| 3                                | -37.969396                   | -37.969397 (Conv.)      |
| 4                                | -37.969396                   | ...                     |
| 5                                | -37.969397 (Conv.)           | ...                     |
| HF (double zeta)                 |                              |                         |
| H <sub>diag</sub>                | 7.22(1)--7.07(4)             | -2.23(2)--4.50(1)       |
| 1                                | NA                           | -100.154141             |
| 2                                | NA                           | -100.160063             |
| 3                                | NA                           | -100.160282             |
| 4                                | NA                           | -100.160287             |
| 5                                | NA                           | -100.160289 (Conv.)     |
| H <sub>2</sub> S (minimal basis) |                              |                         |
| H <sub>diag</sub>                | -3.27(-6)--2.71(7)           | -3.98(1)--1.64(3)       |
| 1                                | NA                           | -397.386385             |
| 2                                | NA                           | -397.387006 (Conv.)     |
| PH <sub>3</sub> (minimal basis)  |                              |                         |
| H <sub>diag</sub>                | -8.06(-6)--1.85(7)           | -3.49(1)--1.44(3)       |
| 1                                | NA                           | -341.357283             |
| 2                                | NA                           | -341.359218             |
| 3                                | NA                           | -341.359238 (Conv.)     |

Table I shows the ICIGSD energies and the dimensions in each iteration of C<sub>2</sub>H<sub>4</sub> with the minimal basis set. This calculation is due to the integral-free algorithm. The dimension and the energy at the first iteration are identical to those of the conventional SDCI since the deexcitation operators applied to the Hartree-Fock function vanish identically in

Eq. (5). The energy of the second iteration was slightly worse by about  $5 \times 10^{-5}$  a.u. than that of the singles, doubles, triples, and quadruples CI (SDTQ-CI). After several iterations, the ICIGSD dimension becomes a constant, i.e., the GSD dimension. In the ethylene case, the dimension became 532 after the third iteration. The ICIGSD energy rapidly converges to the FCI one; only five iterations were necessary for obtaining the microhartree ( $10^{-6}$  a.u.) accuracy. The convergence behaviors of the ICIGSD for other systems were almost the same as those of this example, as far as we used the integral-free algorithm.

Now, we compare the ICIGSD calculations due to the integral-free algorithm and the integral-including algorithm. We used the Householder bisection and the inverse iteration method with double-precision accuracy in the diagonalization step of each iteration. In Table II we gave the iteration processes of these two algorithms for O<sub>3</sub>, CH, HF, H<sub>2</sub>S, and PH<sub>3</sub>. The basis sets are minimal for O<sub>3</sub>, H<sub>2</sub>S, and PH<sub>3</sub> and double zeta for CH and HF. In the integral-including algorithm, the basis functions  $\{|\psi_n\rangle, v_p^r a_r^\dagger a_p |\psi_n\rangle, w_{pq}^{rs} a_r^\dagger a_s^\dagger a_q a_p |\psi_n\rangle\}$  were used. As seen from Table II, the diagonal elements of the Hamiltonian matrices in the integral-including algorithm widely range from the order of  $10^{-6}$  a.u. to the order of  $10^4$  a.u. for the molecules including up to first-row atoms and from the order of  $10^{-6}$  a.u. to the order of  $10^7$  a.u. for the molecules including up to second-row atoms. For this reason, the ICIGSD diagonalization of the integral-including algorithm failed for most of the molecules shown in Table II. For CH, the convergence of the integral-including algorithm was reached later than the integral-free algorithm. On the other hand, in the integral-free algorithm, the ranges of the diagonal elements of the Hamiltonian matrices were much moderate;  $10 \sim 10^2$  a.u. for the molecules including first-row atoms and  $10 \sim 10^3$  a.u. for the molecules including second-row atoms. Therefore, no singularity problem occurs in this case, and the ICIGSD calculations rapidly converge to the FCI.

Now that we have demonstrated how important it is to use the ICIGSD method with the integral-free algorithm, we will perform hereafter the calculations with only the integral-free algorithm.

Table III summarizes the ICIGSD results, together with

TABLE III. ICIGSD and FCI for the ground states of ten molecules with the minimal basis sets.<sup>a</sup>

| Molecule                      | Active space<br>occ. $\times$ unocc. | Hartree-Fock<br>energy<br>(a.u.) | FCI    |                  | ICIGSD |       |                  |
|-------------------------------|--------------------------------------|----------------------------------|--------|------------------|--------|-------|------------------|
|                               |                                      |                                  | Dim.   | Energy<br>(a.u.) | Dim.   | Iter. | Energy<br>(a.u.) |
| H <sub>2</sub> O              | 4 $\times$ 2                         | -75.676507                       | 37     | -75.727911       | 37     | 2     | -75.727911       |
| BH                            | 3 $\times$ 3                         | -25.001486                       | 104    | -25.059317       | 53     | 3     | -25.059317       |
| N <sub>2</sub>                | 5 $\times$ 3                         | -108.541824                      | 396    | -108.700217      | 119    | 4     | -108.700217      |
| HCN                           | 5 $\times$ 4                         | -92.573460                       | 4076   | -92.741207       | 345    | 6     | -92.741207       |
| C <sub>2</sub> H <sub>2</sub> | 5 $\times$ 5                         | -76.602406                       | 8152   | -76.775867       | 289    | 6     | -76.775867       |
| C <sub>2</sub> H <sub>4</sub> | 6 $\times$ 6                         | -77.826602                       | 107952 | -77.991647       | 532    | 5     | -77.991647       |
| CH <sub>3</sub> F             | 7 $\times$ 4                         | -138.472331                      | 54692  | -138.570669      | 993    | 5     | -138.570669      |
| HCHO                          | 6 $\times$ 4                         | -113.440285                      | 11148  | -113.584518      | 494    | 8     | -113.584518      |
| CO <sub>2</sub>               | 8 $\times$ 4                         | -186.852493                      | 30901  | -187.065936      | 506    | 9     | -187.065936      |
| O <sub>3</sub>                | 9 $\times$ 3                         | -223.415852                      | 12126  | -223.679984      | 884    | 7     | -223.679984      |

<sup>a</sup>ICIGSD is due to the integral-free algorithm.

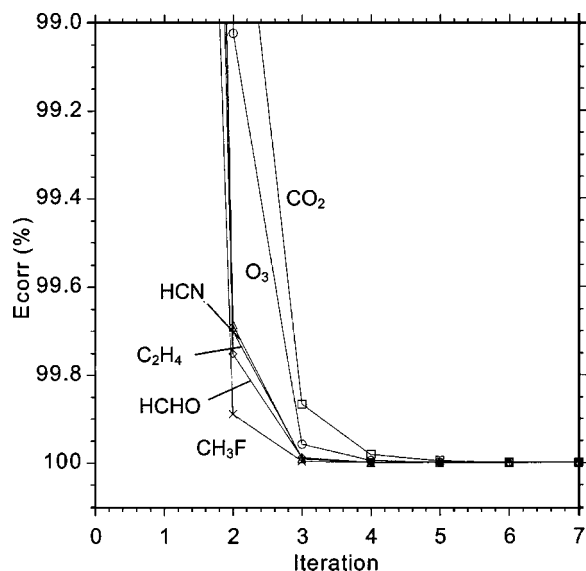


FIG. 1. Convergence behaviors of ICI GSD calculations with the minimal basis sets.

the FCI results, for the ten molecules calculated with the minimal basis sets. In the table, the ICI GSD dimension was given for the final iteration, and the FCI dimension shows the number of the Slater determinants involved. The dimension of the present ICI GSD is in the order of  $(N/2)^2 \times (M - N/2)$ ,<sup>2</sup> where  $N$  and  $M$  are the numbers of electrons and orbitals, respectively, and the difference from the FCI dimension becomes remarkable for large systems. The numbers of iterations for obtaining the accuracy of  $10^{-6}$  a.u. (0.0006 kcal/mol) were three to nine, which were much smaller than those of the SICI and ICI3 reported previously.<sup>7</sup>

The convergence behaviors of the ICI GSD method were shown in Fig. 1 for the minimal basis calculations. Since each iteration of ICI is variational, the energy decreases monotonically and converges to the FCI energy from above. This trend was also observed in the previous SICI and ICI3 calculations.<sup>7</sup> It should be noted that the fast convergence was also obtained for  $O_3$  the ground state of which has a quasidegenerate biradical character. In the SICI and ICI3 cases, the convergence of  $O_3$  was slow in the initial stage of iterations.<sup>7</sup>

Table IV shows the results for the molecules calculated with the double-zeta basis. Again the ICI GSD energies rap-

idly converge to the FCI ones. The numbers of iterations for convergence were quite small, about two to five iterations to get a  $10^{-6}$  a.u. accuracy, and even less than the minimal basis case, though the GSD dimensions became larger here. From these results, we may conclude that the convergence of the ICI GSD calculations are quite fast, irrespective of the quality of the basis set and the size of systems, as far as we take the integral-free algorithm. This result is very encouraging in comparison with the previous SICI and ICI3 calculations. The iteration numbers for convergence would be related to the numbers of the electrons of the system, since in the  $N$ th iteration  $2N$ -electron excitations are generated in the present method.

## B. Open-shell higher-spin states

We have applied the ICI GSD method to various spin multiplicities. Table V shows the results for the doublet to quintet states of  $N_2$  with the limited active space [five occupied and five unoccupied molecular orbitals (MOs)] using double-zeta basis set with  $s$ -type Rydberg function.<sup>25</sup> The ground state of each spin multiplicity was calculated. Since the  $T_n$  operator given in Eq. (5) is totally symmetric, we simply used the initial-guess function of the target spin-space symmetry for obtaining the ICI GSD wave function of the desired symmetry. We adopted single dominant spin-adapted configuration as an initial guess for the doublet to quintet excited states. Again, the ICI GSD method converged to the FCI results after four to six iterations. The ICI GSD dimensions of different spin symmetries were almost the same, since the ICI GSD operators are determined by the structure of the Hamiltonian.

Thus, the ICI GSD method for open-shell and higher-spin multiplicities are as easy as for the closed-shell ground state.

## C. Quasidegenerate states

The performance of the method to the bond dissociation or quasidegenerate states is an important issue. The present method was applied to the ground state of CO along the bond dissociation process, and the result is given in Table VI. As seen from the Hartree-Fock weight, the Hartree-Fock dominant character is lost quickly as the CO length increases. The weight changes as 91.0, 52.1, and 0.8% for  $r=r_e$ ,  $1.5 \times r_e$ , and  $2.0 \times r_e$ , respectively. The ICI GSD calculations were performed using the same quality of basis sets and active

TABLE IV. ICI GSD and FCI for the double-zeta basis sets.<sup>a</sup>

| Molecule                                  | Active space<br>occ. $\times$ unocc. | Hartree-Fock<br>energy<br>(a.u.) | FCI    |                  | ICI GSD |       |                  |
|---|--------------------------------------|----------------------------------|--------|------------------|---------|-------|------------------|
|   |                                      |                                  | Dim.   | Energy<br>(a.u.) | Dim.    | Iter. | Energy<br>(a.u.) |
| Be  | 2 $\times$ 2                         | -14.568534                       | 36     | -14.582693       | 20      | 2     | -14.582693       |
| LiH                                       | 2 $\times$ 10                        | -7.981094                        | 1428   | -8.008682        | 417     | 2     | -8.008682        |
| BH  | 3 $\times$ 9                         | -25.113743                       | 12936  | -25.187657       | 1164    | 3     | -25.187657       |
| CH <sup>+</sup> ( <sup>1</sup> $\Sigma$ ) | 3 $\times$ 9                         | -37.885843                       | 12936  | -37.969397       | 1146    | 3     | -37.969397       |
| CH <sup>+</sup> ( <sup>1</sup> $\Pi$ )    | 3 $\times$ 9                         | -37.761931                       | 12064  | -37.853620       | 1144    | 3     | -37.853620       |
| HF  | 5 $\times$ 7                         | -100.021970                      | 157984 | -100.160289      | 1176    | 5     | -100.160289      |

<sup>a</sup>ICI GSD is due to the integral-free algorithm.

TABLE V. ICI-GSD and FCI for the doublet ionized, doublet electron-attached, triplet, quartet, and quintet states of  $N_2$  with double-zeta basis set.<sup>a</sup>

| State                       | Hartree-Fock<br>energy<br>(a.u.) | FCI  |                  | ICI-GSD |       |                  |
|-----------------------------|----------------------------------|------|------------------|---------|-------|------------------|
|                             |                                  | Dim. | Energy<br>(a.u.) | Dim.    | Iter. | Energy<br>(a.u.) |
| Doublet (ionized)           |                                  |      |                  |         |       |                  |
| $2\Sigma_g^+$               | -107.992338                      | 6716 | -108.214908      | 289     | 6     | -108.214908      |
| Doublet (electron-attached) |                                  |      |                  |         |       |                  |
| $2\Sigma_u^-$               | -108.472335                      | 6716 | -108.641658      | 289     | 6     | -108.641658      |
| Triplet                     |                                  |      |                  |         |       |                  |
| $3\Pi_u$                    | -108.326615                      | 5612 | -108.426040      | 289     | 6     | -108.426040      |
| Quartet                     |                                  |      |                  |         |       |                  |
| $4\Sigma_u^+$               | -107.804890                      | 3120 | -107.949326      | 289     | 5     | -107.949326      |
| Quintet                     |                                  |      |                  |         |       |                  |
| $5\Pi_u$                    | -108.078228                      | 1792 | -108.140790      | 288     | 4     | -108.140790      |

<sup>a</sup>ICI-GSD is due to the integral-free algorithm.

space as in the calculations of  $N_2$ , an isoelectronic molecule. Although the initial guess of the present ICI-GSD calculations was the ground-state Hartree-Fock in all cases, six to eight iterations were enough for obtaining the convergence to FCI. We understand this result because the ICI-GSD method achieves the quality of the SDTQ-CI at the second iteration.

#### D. ICI-CI calculations of the excited states

Finally, we examine the ICI-GSD-CI method for calculating the excited states. Table VII shows the ICI-GSD-CI results for the  $1\Sigma$  and  $1\Pi$  excited states of  $CH^+$  in comparison with the FCI results. The excitation level denotes the number of electrons involved in the excitation process. The ICI-CI wave functions were calculated using the ICI-GSD ground-state wave function converged with the  $10^{-6}$ -hartree accuracy. Method B of Paper II explained above was adopted, and therefore the excited states were described here within the general singles and doubles operators applied to the ICI-GSD wave function of the ground state. As explained in the previous section, the  $1\Sigma$  excited states, whose symmetry is the same as that of the ground state, correspond to the higher solutions of the converged GSD diagonalization, while the  $1\Pi$  excited states were calculated, following the ICI-GSD-CI formalism given in Eq. (13) or (14), because the symmetry of these excited states is different from that of the ground state. Note that only a single diagonalization is necessary in the ICI-CI method; no iteration step is involved as in the SAC-CI method.

As shown in Table VII, the ICI-GSD-CI method reproduced the FCI energies in excellent accuracy regardless of

the excitation levels; the deviations were less than  $10^{-5}$  au for one-electron processes, and the errors for two-electron processes were within  $10^{-4}$  au at most. It is remarkable that the ICI-GSD method with general singles and doubles operators described well the two-electron processes. Further improvement is, of course, possible by using the ICI-GSD-CI general- $R$  method, in which triples and higher operators are added to the GSD operators in the ICI-CI stage for describing the excited states. For other systems calculated in the present study, the accuracy and the performance of the ICI-GSD-CI method were almost the same as those of this example.

#### IV. SUMMARY

The ICI-GSD method lies in a unique position among the ICI formalisms based on the basis-set expansion algorithm. In an ordinary ICI method, it is impossible to formulate the integral-free algorithm; it is possible only in the GSD case is it possible since the second-quantized Hamiltonian consists of the GSD terms, and therefore we can eliminate the elements of the integrals of  $H^3$  that may lead to a divergence due to the singularity of the Coulombic potential of the Hamiltonian. This makes the ICI-GSD method free from the singularity problem that originates from the integrals of  $H^3$ . This was demonstrated by performing the integral-including calculations as a contrast, where the calculations became impossible due to the existence of too large matrix elements within the double-precision accuracy. Another merit of the ICI-GSD is that the number of the variables is GSD, i.e., moderately large in contrast to the SICI or ICI3 performed

TABLE VI. ICI-GSD<sup>a</sup> and FCI for the ground state of CO at  $r=r_e$ ,  $1.5\times r_e$ , and  $2.0\times r_e$ .

| $R_{CO}$        | Hartree-Fock<br>energy<br>(a.u.) | HF weight<br>(%) | FCI   |                  | ICI-GSD |       |                  |
|-----------------|----------------------------------|------------------|-------|------------------|---------|-------|------------------|
|                 |                                  |                  | Dim.  | Energy<br>(a.u.) | Dim.    | Iter. | Energy<br>(a.u.) |
| $r_e$           | -112.334141                      | 91.0             | 16304 | -112.482772      | 538     | 6     | -112.482772      |
| $1.5\times r_e$ | -111.997532                      | 52.1             | 16304 | -112.295416      | 538     | 8     | -112.295416      |
| $2.0\times r_e$ | -111.867560                      | 0.8              | 16304 | -112.150999      | 538     | 6     | -112.150999      |

<sup>a</sup>ICI-GSD is due to the integral-free algorithm.

TABLE VII. ICIGSD-CI and FCI for the  $^1\Sigma$  and  $^1\Pi$  excited states of  $\text{CH}^+$ .

| State       | Excitation level | Character                            | FCI energy (a.u.) | ICIGSD-CI     |                   |
|-------------|------------------|--------------------------------------|-------------------|---------------|-------------------|
|             |                  |                                      |                   | Energy (a.u.) | $\Delta^a$ (a.u.) |
| $1^1\Sigma$ | 0                | ground                               | -37.96940         | -37.96940     | 0.00000           |
| $2^1\Sigma$ | 2                | $\sigma^2 \rightarrow \pi^2$         | -37.70787         | -37.70778     | 0.00009           |
| $3^1\Sigma$ | 2                | $\sigma^2 \rightarrow \pi^2$         | -37.65990         | -37.65989     | 0.00001           |
| $4^1\Sigma$ | 1                | $\sigma \rightarrow \sigma^*$        | -37.43040         | -37.43040     | 0.00000           |
| $5^1\Sigma$ | 2                | $\sigma, 2s \rightarrow \pi^2$       | -37.32862         | -37.32852     | 0.00010           |
| $1^1\Pi$    | 1                | $\sigma \rightarrow \pi$             | -37.85262         | -37.85262     | 0.00000           |
| $2^1\Pi$    | 2                | $\sigma^2 \rightarrow \pi, \sigma^*$ | -37.43836         | -37.43835     | 0.00001           |
| $3^1\Pi$    | 1                | $2s \rightarrow \pi$                 | -37.31875         | -37.31875     | 0.00000           |
| $4^1\Pi$    | 1                | $\sigma \rightarrow \pi$             | -37.30099         | -37.30099     | 0.00000           |

<sup>a</sup>Energy difference between FCI and ICIGSD-CI.

previously, where the numbers of the variables were only one and three, respectively. For this reason, the convergence of the ICIGSD method was remarkably good in contrast to the SICI and ICI3 carried out previously. Thus, the two merits of the ICIGSD originate from the unique GSD structure of the formalism.

The ICIGSD calculations of this paper were mostly done with the integral-free algorithm. It was applied to the various molecular electronic states with minimal and double-zeta basis. It was shown that the convergence of the ICIGSD method is very rapid in contrast to the SICI and ICI3 calculations shown in the previous work,<sup>7</sup> where the integral-free algorithm was impossible. This rapid convergence property was observed regardless of the character of the electronic states and the quality of the basis sets. Though the test calculations were done only for small molecules, the numbers of electrons are expected to be closely related with the convergence rate from the structure of the ICIGSD wave function. The ICIGSD method is applicable to various spin multiplicities simply by adopting the initial guess function belonging to the desired spin symmetry, since the excitation operators in  $T_n$  are totally symmetric. The method is also shown to be useful for the quasidegenerate states and bond dissociation processes.

The ICIGSD-CI method was also examined for calculating molecular excited states simultaneously with Method B reported in Paper II.<sup>3</sup> We examined both one- and two-electron excited states and confirmed that the ICIGSD-CI method reproduces the FCI results in good accuracy.

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